Thermodynamics of the multi-component dimerizing hard-sphere Yukawa mixture in the associative mean spherical approximation.

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Abstract

Explicit analytical expressions for Helmholtz free energy, chemical potential, entropy and pressure of the multi-component dimerizing Yukawa hard-sphere fluid are presented. These expressions are written in terms of the Blum's scaling parameter Γ, which follows from the solution of the associative mean spherical approximation (AMSA) for the model with factorized Yukawa coefficients. In this case solution of the AMSA reduces to the solution of only one nonlinear algebraic equation for Γ. This feature enables the theory to be used in the description of the thermodynamical properties of associating fluids with arbitrary number of components, including the limiting case of polydisperse fluids.

1 Introduction

Much of the progress achieved by the liquid-state integral-equation theories is due to the availability of the integral-equation approximations (IEA), which are amenable to the analytical solution for a number of the models of dense fluids and liquids. Since 1963, when Percus-Yevick approximation for the hard-sphere fluid was solved analytically [1, 2], the analytical solutions were derived for a large variety of non-trivial Hamiltonian models (see [3, 4] and references therein). During the last two decades substantial efforts have been focused on the development of the analytically solvable IEA for the models of associating fluids [4]. Most of these studies were carried out in the frames of the product-reactant Ornstein-Zernike approach (PROZA) [5, 6, 7, 8, 9, 10, 11, 12, 13, 14, 15, 16, 17, 18] for the models, which combine hard-sphere interaction and sticky interaction due to a certain number of the sticky points located on the surface of each hard sphere. Different versions of the models, which describe dimerizing [7, 8, 9], polymerizing [10, 11, 12, 13, 14, 15] and network forming [16, 17, 18] fluids, where investigated . More recently these studies were extended by adding a van der Waals attraction, modeled by a sum of the Yukawa terms [19, 20, 21, 22]. The properties of the corresponding models were studied using the analytical solution of the associating mean spherical approximation (AMSA) [23]. In the particular case of the multi-component Yukawa dimerizing hard-sphere fluid with factorizable Yukawa coefficients the Yukawa part of the solution was reduced to the solution of only one nonlinear algebraic equation for the Blum's [24, 25] scaling parameter Γ [26, 20]. In the limiting case of complete association, when the system is represented by the multi-component mixture of Yukawa heteronuclear hard-sphere diatomics, solution of this equation represents full solution of the AMSA. In this limit PROZA reduces to the 'proper' site-site theory [27] due to Chandler et al. [28].

In this article we extend solution of the AMSA obtained earlier [19, 20] and derive explicit expressions for the thermodynamical properties of the multi-component Yukawa dimerizing hard-sphere fluid in terms of the Γ-parameter.

2 The model

We consider M-component mixture of dimerizing Yukawa hard spheres of species $i = 1, 2, \ldots, M$ with diameters σ_i and densities ρ_i. Each of the hard spheres has one sticky site placed on a surface. The pair potential of the model consists of the hard-sphere term, sticky site-site term and Yukawa term $\Phi_{ij}^{(Y)}(r)$, which was chosen to be of the following form:

$$\beta\Phi_{ij}^{(Y)}(r) = -\frac{K_{ij}}{r}e^{-zr} \tag{1}$$

where $\beta = 1/kT$, k is the Boltzmann constant, T is the absolute temperature and r is the distance between the centers of the spheres.

3 Solution of the AMSA

Solution of the AMSA for the model at hand was obtained earlier [19, 20] and we shall therefore omit the details here and present only the final expressions, which are needed in our derivation of the thermodynamics.

AMSA consists of the two-density Ornstein-Zernike equation

$$\hat{\mathbf{h}}_{ij}(k) = \hat{\mathbf{c}}_{ij}(k) + \sum_l \rho_l \hat{\mathbf{c}}_{il}(k)\boldsymbol{\alpha}_l \hat{\mathbf{h}}_{lj}(k), \tag{2}$$

supplemented by the MSA-like closure conditions

$$\mathbf{c}_{ij}(r) = \mathbf{E}\frac{K_{ij}}{r}e^{-zr}, \qquad r > \sigma_{ij} = (\sigma_i + \sigma_j)/2 \tag{3}$$

$$\mathbf{h}_{ij}(r) = -\mathbf{E} + \frac{\mathbf{t}_{ij}}{2\pi\sigma_{ij}}\delta(r - \sigma_{ij}), \qquad r < \sigma_{ij}. \tag{4}$$

Here $\hat{\mathbf{h}}_{ij}(k)$, $\hat{\mathbf{c}}_{ij}(k)$, $\mathbf{t}_{ij}$, $\boldsymbol{\alpha}_i$ and $\mathbf{E}$ are the following matrices:

$$\hat{\mathbf{h}}_{ij}(k) = \begin{pmatrix} \hat{c}_{i_0j_0}(k) & \hat{c}_{i_0j_1}(k) \\ \hat{c}_{i_1j_0}(k) & \hat{c}_{i_1j_1}(k) \end{pmatrix}, \qquad \hat{\mathbf{c}}_{ij}(k) = \begin{pmatrix} \hat{c}_{i_0j_0}(k) & \hat{c}_{i_0j_1}(k) \\ \hat{c}_{i_1j_0}(k) & \hat{c}_{i_1j_1}(k) \end{pmatrix},$$

$$\mathbf{t}_{ij} = \begin{pmatrix} 0 & 0 \\ 0 & t_{i_1j_1} \end{pmatrix}, \qquad \boldsymbol{\alpha}_i = \begin{pmatrix} 1 & \alpha_i \\ \alpha_i & 0 \end{pmatrix}, \qquad \mathbf{E} = \begin{pmatrix} 1 & 0 \\ 0 & 0 \end{pmatrix},$$

where $\hat{h}_{i_\alpha j_\beta}(k)$ and $\hat{c}_{i_\alpha j_\beta}(k)$ are Fourier transforms of the total $h_{i_\alpha j_\beta}(r)$ and direct $c_{i_\alpha j_\beta}(r)$ correlation functions, respectively, $t_{i_1 j_1} = T_{ij} g_{i_0 j_0}(\sigma_{ij}^+)$, $g_{i_0 j_0}(\sigma_{ij}^+)$ is the contact value of the radial distribution function $g_{i_\alpha j_\beta}(r) = h_{i_\alpha j_\beta}(r) + \delta_{\alpha 0}\delta_{\beta 0}$, T_{ij} is the parameter which defines the strength of the sticky interaction and α_i is the fraction of non bonded particles. Here the lower indices α and β denote the bonding state of the corresponding particle and take the values 0 (non bonded) and 1 (bonded). Fraction of non bonded particles α_i together with association strength parameter T_{ij} obey the mass action law (MAL) relation

$$1 = \alpha_i \left(1 + 2 \sum_j \rho_j \sigma_{ij} \alpha_j t_{i_1 j_1} \right). \tag{5}$$

Solution of the AMSA was obtained using Baxter factorization method [29] with the general scheme of the solution based upon the version of factorization technique developed by Høye and Blum [30, 31]. According to Baxter [29] the OZ equation (2) can be factorized as

$$\mathbf{S}_{ij}(|r|) = \mathbf{Q}_{ij}(r) - \sum_l \rho_l \int dr' \mathbf{Q}_{il}(r') \boldsymbol{\alpha}_l \mathbf{Q}_{jl}^T(r' - r), \tag{6}$$

$$\mathbf{J}_{ij}(|r|) = \mathbf{Q}_{ij}(r) + \sum_l \rho_l \int dr' \mathbf{J}_{il}(|r' - r|) \boldsymbol{\alpha}_l \mathbf{Q}_{lj}(r'), \tag{7}$$

where T denotes the transpose matrix and the integrals $\mathbf{S}_{ij}(r) = 2\pi \int_r^\infty dr' r' \mathbf{c}_{ij}(r')$ and $\mathbf{J}_{ij}(r) = 2\pi \int_r^\infty dr' r' \mathbf{h}_{ij}(r')$ satisfy the following boundary conditions:

$$\begin{cases} \mathbf{J}_{ij}(r) &= \pi r^2 \mathbf{E} + \mathbf{J}_{ij}, & r \le \sigma_{ij} \\ \mathbf{S}_{ij}(r) &= \mathbf{E} \frac{K_{ij}}{z} e^{-zr}, & r > \sigma_{ij} \end{cases}. \tag{8}$$

Here $\mathbf{J}_{ij} = \mathbf{J}_{ij}(0)$. From the analysis of the equations (6) and (7) we get [20]

$$\mathbf{Q}_{ij}(r) = \left[\mathbf{q}_{ij}(r) + \mathbf{t}_{ij} \right] \theta(\sigma_{ij} - r) + \tilde{\mathbf{E}}^T \tilde{\mathbf{D}}_{ij} e^{-zr}, \qquad r > \lambda_{ji}, \tag{9}$$

where $\lambda_{ij} = \frac{1}{2}(\sigma_i - \sigma_j)$, $\tilde{\mathbf{D}}_{ij}$ and $\tilde{\mathbf{E}}$ are the row vectors, i.e. $\tilde{\mathbf{D}}_{ij} = (D_{i_0 j_0}, D_{i_0 j_1})$, $\tilde{\mathbf{E}} = (1, 0)$. Vector $\tilde{\mathbf{D}}_{ij}$ satisfies the following relation

$$\frac{2\pi}{z} \tilde{\mathbf{K}}_{ij} = \sum_l \rho_l \tilde{\mathbf{D}}_{il} \boldsymbol{\alpha}_l \hat{\mathbf{Q}}_{jl}^T(iz), \tag{10}$$

where $\hat{\mathbf{Q}}_{ij}(k) = \delta_{ij} (\rho_j \boldsymbol{\alpha}_j)^{-1} - 2\pi \int_{\lambda_{ji}}^\infty dr\ \mathbf{Q}_{ij}(r) e^{ikr}$ and $\tilde{\mathbf{K}}_{ij} = (K_{ij}, 0)$. Expression for $\mathbf{q}_{ij}(r)$ in the interval $\lambda_{ji} < r < \sigma_{ij}$ is

$$\mathbf{q}_{ij}(r) = \frac{1}{2} \tilde{\mathbf{E}}^T \tilde{\mathbf{A}}_j (r - \sigma_{ij})(r - \lambda_{ji}) + \tilde{\mathbf{E}}^T \tilde{\boldsymbol{\beta}}_j (r - \sigma_{ij}) + \mathbf{C}_{ij} \left(e^{-zr} - e^{-z\sigma_{ij}} \right). \tag{11}$$

Here

$$\tilde{\boldsymbol{\beta}}_j = \frac{\pi}{\Delta}\sigma_j \tilde{\mathbf{E}} + \frac{2\pi}{\Delta}\sum_n \tilde{\boldsymbol{\mu}}_j^{(n)}, \quad \tilde{\mathbf{A}}_j = \frac{2\pi}{\Delta}\left(\tilde{\mathbf{E}} + \frac{1}{2}\zeta_2\tilde{\boldsymbol{\beta}}_j + \sum_n \tilde{\mathbf{M}}_j^{(n)} - \tilde{\boldsymbol{\tau}}_j\right), \tag{12}$$

$$\mathbf{C}_{ij} = \sum_l \boldsymbol{\gamma}_{il}(z)\tilde{\mathbf{E}}^T\tilde{\mathbf{D}}_{lj} - \tilde{\mathbf{E}}^T\tilde{\mathbf{D}}_{ij}, \tag{13}$$

where

$$s\boldsymbol{\gamma}_{ij}(s) = 2\pi\rho_j\mathbf{G}_{ij}(s)\boldsymbol{\alpha}_j, \quad \left(\mathbf{G}_{ij}(s) = \int_0^\infty dr'r'\mathbf{g}_{ij}(r')e^{-sr'}\right), \tag{14}$$

$$\tilde{\boldsymbol{\mu}}_j^{(n)} = \sum_l \rho_l\tilde{\mathbf{C}}_l^\mu(z)\boldsymbol{\alpha}_l\tilde{\mathbf{E}}^T\tilde{\mathbf{D}}_{lj}^{(n)}e^{-z\sigma_{lj}}, \quad \tilde{\mathbf{M}}_j^{(n)} = \sum_l \rho_l\tilde{\mathbf{C}}_l^M(z)\boldsymbol{\alpha}_l\tilde{\mathbf{E}}^T\tilde{\mathbf{D}}_{lj}^{(n)}e^{-z\sigma_{lj}}, \tag{15}$$

$$\tilde{\mathbf{C}}_l^\mu(s) = \sum_k \tilde{\mathbf{E}}\boldsymbol{\gamma}_{lk}^T(s)e^{s\sigma_{lk}}s\sigma_k^3\phi_1(\sigma_k s) + \frac{1}{s^2}\left(1 + \frac{1}{2}s\sigma_l\right)\tilde{\mathbf{E}}, \tag{16}$$

$$\tilde{\mathbf{C}}_l^M(s) = \sum_k \tilde{\mathbf{E}}\boldsymbol{\gamma}_{lk}^T(s)e^{s\lambda_{lk}}\sigma_k^2 s\varphi_1(-s\sigma_k) - \frac{1+s\sigma_l}{s}\tilde{\mathbf{E}}. \tag{17}$$

Here $\boldsymbol{\gamma}_{ij}(z)$ satisfies the following set of the algebraic equations

$$\sum_l z\boldsymbol{\gamma}_{il}(z)\hat{\mathbf{Q}}_{lj}(iz) = \tilde{\mathbf{E}}\left[\tilde{\mathbf{A}}_j\left(1 + \frac{1}{2}z\sigma_i\right) + \tilde{\boldsymbol{\beta}}_j z\right]\frac{e^{-z\sigma_{ij}}}{z^2} - \mathbf{C}_{ij}e^{-2z\sigma_{ij}} + \mathbf{t}_{ij}e^{-z\sigma_{ij}} \tag{18}$$

and

$$\tilde{\boldsymbol{\tau}}_j = \sum_l \rho_l\sigma_l\tilde{\mathbf{E}}\boldsymbol{\alpha}_l\mathbf{t}_{lj}, \quad \zeta_m = \sum_l \rho_l\sigma_l^m, \quad \Delta = 1 - \frac{\pi}{6}\zeta_3, \tag{19}$$

$$\varphi_1(x) = \frac{1 - x - e^{-x}}{x^2}, \quad \phi_1(x) = \frac{1}{x^3}\left[1 - \frac{1}{2}x - \left(1 + \frac{1}{2}x\right)e^{-x}\right].$$

One can see that all coefficients of the factor function $\mathbf{Q}(r)$ are determined by the set of unknowns $\tilde{\mathbf{D}}_{ij}$ and $\boldsymbol{\gamma}_{ij}(z)$. These unknowns follow from the solution of the set of equations (10) and (18).

Substantial simplification of the final algebraic equations representing the solution of the AMSA occurs in the case of factorizable Yukawa coefficients, i.e. for $K_{ij} = Kd_id_j$. According to Eq. (10) now $\tilde{\mathbf{D}}_{ij}$ can be written in the following form

$$\tilde{\mathbf{D}}_{ij} = -d_i\tilde{\mathbf{a}}_j e^{\frac{1}{2}z\sigma_j}, \tag{20}$$

which gives

$$\mathbf{C}_{ij} = \left(d_i\tilde{\mathbf{E}}^T - \frac{1}{z}\tilde{\mathbf{B}}_i^T\right)\tilde{\mathbf{a}}_j e^{\frac{1}{2}z\sigma_j}, \tag{21}$$

$$\tilde{\boldsymbol{\beta}}_j = \frac{\pi}{\Delta}\sigma_j\tilde{\mathbf{E}} + \Delta_1\tilde{\mathbf{a}}_j, \tag{22}$$

$$\tilde{\mathbf{A}}_j = \frac{2\pi}{\Delta}\left(1+\frac{\pi}{2\Delta}\zeta_2\sigma_j\right)\tilde{\mathbf{E}} + \frac{\pi}{\Delta}P\tilde{\mathbf{a}}_j - \frac{2\pi}{\Delta}\tilde{\boldsymbol{\tau}}_j. \tag{23}$$

Here

$$\tilde{\mathbf{B}}_i = z\sum_l \tilde{\mathbf{E}}\boldsymbol{\gamma}_{il}^T(z)d_l, \tag{24}$$

$$\Delta_1 = -\frac{2\pi}{\Delta}\tilde{\mathbf{E}}\sum_l \rho_l\boldsymbol{\alpha}_l\sigma_l^2\left[\phi_1(z\sigma_l)\sigma_l\tilde{\mathbf{B}}_l^T e^{\frac{1}{2}z\sigma_l} + \frac{1+z\sigma_l/2}{\sigma_l^2 z^2}d_l\tilde{\mathbf{E}}^T e^{-\frac{1}{2}z\sigma_l}\right], \tag{25}$$

$$P = \left(\zeta_2 - \frac{\Delta}{\pi}z\right)\Delta_1 + \tilde{\mathbf{E}}\sum_l \rho_l\boldsymbol{\alpha}_l\sigma_l\left[\varphi_0(z\sigma_l)\sigma_l\tilde{\mathbf{B}}_l^T e^{\frac{1}{2}z\sigma_l} + d_l\tilde{\mathbf{E}}^T e^{-\frac{1}{2}z\sigma_l}\right], \tag{26}$$

where $\varphi_0(x) = (1-e^{-x})/x$. Next, making use of the symmetry property of the factor function, i.e. $\mathbf{Q}_{ij}(\lambda_{ji}) = \mathbf{Q}_{ji}^T(\lambda_{ij})$, we have

$$\tilde{\mathbf{X}}_i^T\tilde{\mathbf{a}}_j = \tilde{\mathbf{a}}_i^T\tilde{\mathbf{X}}_j, \tag{27}$$

where

$$\tilde{\mathbf{X}}_i^T = \tilde{\mathbf{E}}^T\left(\sigma_i\Delta_1 + d_i e^{-\frac{1}{2}z\sigma_i}\right) + \sigma_i\tilde{\mathbf{B}}_i^T\varphi_0(z\sigma_i)e^{\frac{1}{2}z\sigma_i}. \tag{28}$$

Equation (27) enables us to introduce scaling parameter Γ via the following relation

$$\tilde{\mathbf{a}}_j = \frac{2\Gamma}{D}\tilde{\mathbf{X}}_j, \tag{29}$$

where $D = \sum_k \rho_k\tilde{\mathbf{X}}_k\boldsymbol{\alpha}_k\tilde{\mathbf{X}}_k^T$. Differentiating (6) with respect to r and taking the limit $r \to 0$ we have

$$\tilde{\mathbf{a}}_i = \frac{2}{D}\left[-\tilde{\mathbf{E}}\Delta_1\left(1+\frac{1}{2}z\sigma_i\right) - \tilde{\mathbf{B}}_i e^{\frac{1}{2}z\sigma_i} - \sigma_i\tilde{\mathbf{E}}\eta^B + \sum_k \rho_k\tilde{\mathbf{X}}_k\boldsymbol{\alpha}_k\mathbf{t}_{ik}\right], \tag{30}$$

where

$$\eta^B = \frac{\pi}{2\Delta}\sum_k \rho_k\sigma_k\tilde{\mathbf{X}}_k\boldsymbol{\alpha}_k\tilde{\mathbf{E}}^T. \tag{31}$$

Now all the unknowns of the problem can be expressed in terms of Γ, i.e.

$$X_{i_0} = -\lambda_i - \eta_i\Delta_1 - \frac{2\Delta}{\pi}\xi_i\eta^B, \tag{32}$$

$$X_{i_1} = T_i^\eta\Delta_1 + \frac{2\Delta}{\pi}T_i^\xi\eta^B + T_i^\lambda, \tag{33}$$

where $\pi\sigma_i T_i^y = -2\Delta\xi_i\sum_k \rho_k\alpha_k t_{i_1k_1}y_k$, $(y = \eta, \xi, \lambda)$,

$$\lambda_i = -\frac{d_i e^{-\frac{1}{2}z\sigma_i}}{1+\varphi_0(z\sigma_i)\sigma_i\Gamma}, \qquad \eta_i = \frac{\sigma_i^3 z^2\phi_1(z\sigma_i)}{1+\varphi_0(z\sigma_i)\sigma_i\Gamma}, \qquad \xi_i = \frac{\pi}{2\Delta}\frac{\sigma_i^2\varphi_0(z\sigma_i)}{1+\varphi_0(z\sigma_i)\sigma_i\Gamma},$$

$$\eta^B = \frac{-\frac{\pi}{\Delta}\Theta^\eta\Omega^\lambda + \Theta^\lambda\left(\frac{1}{2}z^2 + \frac{\pi}{\Delta}\Omega^\eta\right)}{\Theta^\eta\left(2\Gamma + \frac{\pi}{\Delta}\zeta_2 + z + 2\Omega^\xi\right) + \frac{\Delta}{\pi}\left(z^2 + \frac{2\pi}{\Delta}\Omega^\eta\right)\left(1-\Theta^\xi\right)}, \tag{34}$$

$$\Delta_1 = \frac{2\Omega^\lambda\left(\Theta^\xi - 1\right) - \left[2\Gamma + \frac{\pi}{\Delta}\zeta_2 + z + 2\Omega^\xi\right]\Theta^\lambda}{\Theta^\eta\left(2\Gamma + \frac{\pi}{\Delta}\zeta_2 + z + 2\Omega^\xi\right) + \frac{\Delta}{\pi}\left(z^2 + \frac{2\pi}{\Delta}\Omega^\eta\right)\left(1-\Theta^\xi\right)}, \tag{35}$$

$$\Omega^y = \sum_l \rho_l\left[\alpha_l T_l^y - y_l\left(1 - \alpha_l\tau_{l_1}\right)\right], \qquad \Theta^y = \sum_l \rho_l\sigma_l\left(\alpha_l T_l^y - y_l\right). \tag{36}$$

Finally, the nonlinear algebraic equation for Γ, which follows from (10), is

$$(\Gamma)^2 + z\Gamma + \pi K D = 0. \tag{37}$$

Full solution of the problem requires solution of the set of equations formed by equations (5) and (37). The former equation needs as an input the contact values of the radial distribution function $g_{i_0j_0}$. Corresponding expression follows from (7)

$$g_{i_0j_0} \equiv g_{i_0j_0}\left(r \to \sigma_{ij}^+\right) = \left(\frac{1}{\Delta} + \frac{\xi_2\sigma_i\sigma_j}{4\Delta^2\sigma_{ij}}\right)\exp\left(\frac{K}{\sigma_{ij}}X_{i_0}^T X_{j_0}\right). \tag{38}$$

Here we have used exponential approximation [32].

4 Thermodynamics

Thermodynamic properties of the model at hand will be calculated via the energy route, which appears to be the most accurate for the MSA-type of the theories. Using standard expression for the excess internal energy in terms of the radial distribution functions, we have

$$\beta\Delta E^Y = -K\sum_i \rho_i d_i \mathbf{E}\boldsymbol{\alpha}_i\tilde{\mathbf{B}}_i^T. \tag{39}$$

Before proceeding to Helmholtz free energy calculations we will prove the following two useful relations

$$\left[\frac{\partial\Delta E^Y}{\partial\left(\rho_i\alpha_i\rho_j\alpha_j t_{i_1j_1}\right)}\right]_{\Gamma=const} = -\frac{K}{\beta}X_{i_0}X_{j_0}, \tag{40}$$

$$\left[\frac{\partial\Delta E^Y}{\partial\Gamma}\right]_{\rho_p=const} = -\frac{1}{\pi\beta}\left(\Gamma^2 + z\Gamma\right), \tag{41}$$

where ρ_p denotes the set of all products $\rho_i\alpha_i\rho_j\alpha_j t_{i_1j_1}$. First of these relations can be derived by substituting $\tilde{\mathbf{B}}_i$ from (28) into (39) and differentiating it with respect

to $\rho_i\alpha_i\rho_j\alpha_j t_{i_1j_1}$ with Γ held constant. We will skip these straightforward calculations and proceed to the second of these relations. To prove relation (41) we start eliminating $\tilde{\mathbf{X}}_i$ from (28), (30) and (29) to get

$$\tilde{\mathbf{B}}_i e^{\frac{1}{2}z\sigma_i}\left(1+\sigma_i\Gamma\varphi_0\left(z\sigma_i\right)\right)=$$

$$-\tilde{\mathbf{E}}\Delta_1\left(1+\frac{1}{2}z\sigma_i+\sigma_i\Gamma\right)-\tilde{\mathbf{E}}\Gamma d_i e^{-\frac{1}{2}z\sigma_i}-\sigma_i\tilde{\mathbf{E}}\eta+\sum_k\rho_k\tilde{\mathbf{X}}\boldsymbol{\alpha}_k\mathbf{t}_{ik}. \tag{42}$$

After substituting (32) into the above equation and performing some lengthy algebra we obtain the following matrix equation for $\tilde{\mathbf{B}}_i$

$$\sum_k\tilde{\mathbf{B}}_k\hat{\mathbf{M}}_{ki}=\left(\left\{1+\frac{1}{2}z\sigma_i+\sigma_i\Gamma+\frac{\pi\sigma_i}{2\Delta}\zeta_2\right\}\tilde{\mathbf{E}}-\tilde{\boldsymbol{\tau}}_{ik}\right)\frac{2\pi}{\Delta z^2}\sum_l\rho_l\left(1+\frac{1}{2}z\sigma_l\right)d_l e^{-\frac{1}{2}z\sigma_l}$$

$$-\tilde{\mathbf{E}}\frac{\pi\sigma_l}{2\Delta}\sum_k\rho_k\sigma_k d_k e^{-\frac{1}{2}z\sigma_k}-\tilde{\mathbf{E}}d_i e^{-\frac{1}{2}z\sigma_i}\Gamma+\tilde{\mathbf{J}}\left[-\sum_k\rho_k\alpha_k t_{i_1j_1}\lambda_k\right. \tag{43}$$

$$\left.+\frac{2\pi}{\Delta z^2}\sum_k\rho_k\left(1+\frac{1}{2}z\sigma_k\right)d_k e^{-\frac{1}{2}z\sigma_k}\sum_l\rho_l\alpha_l t_{i_1j_1}\chi_l-\sum_k\rho_k\sigma_k d_k e^{-\frac{1}{2}z\sigma_k}\sum_l\rho_l\alpha_l t_{i_1l_1}\xi_l\right]$$

where $\tilde{\mathbf{J}}=(0,\quad 1)$, $\hat{\mathbf{M}}_{ki}=e^{\frac{1}{2}z\sigma_k}\left(1+\varphi_0\left(z\sigma_k\right)\sigma_k\Gamma\right)\hat{\mathbf{P}}_{ki}$,

$$\chi_i=\frac{\sigma_i\left\{1+\frac{1}{2}z\sigma_i+\sigma_i\Gamma+\frac{\pi\sigma_i}{2\Delta}\zeta_2\right\}\varphi_0\left(z\sigma_i\right)}{1+\varphi_0\left(z\sigma_i\right)\sigma_i\Gamma}, \tag{44}$$

and $\hat{\mathbf{P}}$ is the Jacobi type of the matrix, i.e. $\hat{\mathbf{P}}_{ki}=\delta_{ik}\hat{\mathbf{I}}+\tilde{\mathbf{c}}_k^T\tilde{\mathbf{d}}_i+\tilde{\mathbf{e}}_k^T\tilde{\mathbf{f}}_i$. Four vectors $\tilde{\mathbf{c}}$, $\tilde{\mathbf{d}}$, $\tilde{\mathbf{e}}$ and $\tilde{\mathbf{f}}$, that form the Jacobi matrix, are

$$\tilde{\mathbf{c}}_i=\rho_i\xi_i\left(1,\quad\alpha_i\right),\quad\tilde{\mathbf{d}}_i=\left(\sigma_i,\quad-\frac{\sigma_i T_i^{\xi}}{\xi_i}\right),\quad\tilde{\mathbf{e}}_i=-\frac{2\pi\rho_i}{\Delta z^2}\eta_i\left(1,\quad\alpha_i\right),$$

$$\tilde{\mathbf{f}}_i=\left(\left\{1+\frac{1}{2}z\sigma_i+\sigma_i\Gamma+\frac{\pi\sigma_i}{2\Delta}\zeta_2\right\},\quad-\tau_{i_1}+\sum_l\rho_l\alpha_l t_{i_1l_1}\chi_l\right),\qquad\hat{\mathbf{I}}=\begin{pmatrix}1&0\\0&1\end{pmatrix}.$$

Corresponding equation for $\left[\frac{\partial\tilde{\mathbf{B}}_i}{\partial\Gamma}\right]_{\rho_p}$ follows from (43) upon its differentiation with respect to Γ

$$\sum_k\left[\frac{\partial\tilde{\mathbf{B}}_k}{\partial\Gamma}\right]_{\rho_p}\hat{\mathbf{M}}_{ki}=-\tilde{\mathbf{X}}_i-\tilde{\mathbf{J}}\left(\frac{2\Delta}{\pi}\sum_k\rho_k\alpha_k t_{i_1k_1}\frac{\xi_k}{\sigma_k}X_{k_0}\right). \tag{45}$$

Taking derivative of the both sides of equation (39) with respect to Γ, using expression for $\left[\frac{\partial\tilde{\mathbf{B}}_i}{\partial\Gamma}\right]_{\rho_p}$, obtained from the solution of the set of equations (45) and taking

into account equation (37), we recover relation (41). Inverse matrix $\hat{\mathbf{M}}_{ki}^{-1}$ together with Γ derivatives, which are used in our calculations, are given in the Appendix.

We start our derivation of the expression for Helmholtz free energy with the following standard thermodynamic relation:

$$\frac{\partial}{\partial \beta}\left(\beta \Delta A\right) = \beta \Delta E. \tag{46}$$

Integrating this equality by parts and using the fact that all thermodynamic quantities according AMSA depend only on one parameter Γ, we have

$$\beta \Delta A^Y = \beta \Delta E^Y - \int_0^{\Gamma} d\Gamma' \beta' \frac{d\Delta E^Y}{d\Gamma'}, \tag{47}$$

where ΔA^Y represent Yukawa contribution to Helmholtz free energy. We start with the system of dimerizing hard spheres and charge it by the Yukawa charge d_i up to the current conditions. Full derivative under the integral in (47) can be expressed in terms of the partial derivatives giving

$$\beta \Delta A^Y = \beta \Delta E^Y - \int_0^{\Gamma} d\Gamma' \beta' \left[\frac{\partial \Delta E^Y}{\partial \Gamma'}\right]_{\rho_p} - \int_0^{\Gamma} d\Gamma' \beta' \sum_{ij} \left[\frac{\partial \Delta E^Y}{\partial \rho_i \alpha_i \rho_j \alpha_j t_{i_1 j_1}}\right]_{\Gamma'} \frac{\partial \rho_i \alpha_i \rho_j \alpha_j t_{i_1 j_1}}{\partial \Gamma'}. \tag{48}$$

Integrating the second integral in (48) by parts and using (40) and (41), we get

$$\beta \Delta A^Y = \beta \Delta E^Y + \frac{1}{\pi}\left(\frac{\Gamma^3}{3} + z\frac{\Gamma^2}{2}\right)$$
$$+ K \sum_{ij} \rho_i \alpha_i \rho_j \alpha_j t_{i_1 j_1} X_{i_0} X_{j_0} - \sum_{ij} \int_0^{\Gamma} d\Gamma' \rho_i \alpha_i \rho_j \alpha_j t_{i_1 j_1} \frac{\partial \left(K X_{i_0} X_{j_0}\right)}{\partial \Gamma'}. \tag{49}$$

Since $\partial t_{j_1 k_1}/\partial \Gamma = t_{j_1 k_1} \partial \ln\left(g_{j_0 k_0}\right)/\partial \Gamma$ and due to the exponential approximation (38) and MAL relation (5) it is straightforward to show that

$$\frac{\partial\ \beta A^{MAL}}{\partial \Gamma} = -\sum_{ij} \rho_i \alpha_i \rho_j \alpha_j t_{i_1 j_1} \frac{\partial\ K X_{i_0} X_{j_0}}{\partial \Gamma}, \tag{50}$$

where

$$\beta \Delta A^{MAL} = \sum_i \ln\ \alpha_i + \sum_{ij} \rho_i \alpha_i \rho_i \alpha_j t_{i_1 j_1}. \tag{51}$$

The final expression for Helmholtz free energy in excess to Helmholtz free energy of dimerizing hard-spheres system is obtained combining (49) and (50)

$$\beta \Delta A^Y = \beta \Delta E^Y + \frac{1}{\pi}\left(\frac{\Gamma^3}{3} + z\frac{\Gamma^2}{2}\right) + K \sum_{ij} \rho_i \alpha_i \rho_j \alpha_j t_{i_1 j_1} X_{i_0} X_{j_0} + \beta \Delta A^{MAL} - \beta \Delta A_0^{MAL}, \tag{52}$$

where

$$\beta \Delta A_0^{MAL} = \sum_i \ln\ \alpha_i^0 + \sum_{ij} \rho_i \alpha_i^0 \rho_j \alpha_j^0 \sigma_{ij} t^0_{i_1 j_1}. \tag{53}$$

In the case of the reference system represented by the multicomponent hard-sphere mixture we have

$$\beta \Delta A = \beta \Delta E + \frac{1}{\pi}\left(\frac{\Gamma^3}{3} + z\frac{\Gamma^2}{2}\right) + K\sum_{ij} \rho_i \alpha_i \rho_j \alpha_j t_{i_1 j_1} X_{i_0} X_{j_0} + \beta \Delta A^{MAL}, \tag{54}$$

with ΔA being Helmholtz free energy in excess to the hard-sphere Helmholtz free energy. Corresponding expression for the excess entropy ΔS is found differentiating (54) with respect to the temperature

$$\Delta S = -\frac{k_B}{\pi}\left(\frac{\Gamma^3}{3} + z\frac{\Gamma^2}{2}\right) - k_B \beta \Delta A^{MAL} - k_B K \sum_{ij} \rho_i \alpha_i \rho_j \alpha_j t_{i_1 j_1} X_{i_0} X_{j_0}. \tag{55}$$

Similar as in the earlier studies [32, 33] the scaling parameter Γ of our theory minimizes the excess Helmholtz free energy

$$\beta \frac{\partial}{\partial \Gamma} \Delta A = 0. \tag{56}$$

Differentiating (54) with respect to the density of one of the components ρ_l, we get expression for the chemical potential

$$\begin{aligned} \beta \Delta \mu_l = {} & \beta \left[\frac{\partial \Delta E}{\partial \rho_l}\right]_\beta + \frac{1}{\pi}\left(\Gamma^2 + z\Gamma\right)\left[\frac{\partial \Gamma}{\partial \rho_l}\right]_\beta + \beta\left[\frac{\partial A^{MAL}}{\partial \rho_l}\right]_\beta \\ & + K\sum_{ij}\left(\left[\frac{\partial \rho_i \alpha_i \rho_j \alpha_j t_{i_1 j_1}}{\partial \rho_l}\right]_\beta X_{i_0} X_{j_0} + \rho_i \alpha_i \rho_j \alpha_j t_{i_1 j_1}\left[\frac{\partial X_{i_0} X_{j_0}}{\partial \rho_l}\right]_\beta\right). \end{aligned} \tag{57}$$

Using (5) and (38), it can be shown that

$$\beta \frac{\partial \Delta A^{MAL}}{\partial \rho_l} = \ln \alpha_l - \sum_{ij} \rho_i \alpha_i \rho_j \alpha_j t_{i_1 j_1}\left(\sigma_{ij}\left[\frac{\partial \ln g_{ij}^{HS}(\sigma_{ij})}{\partial \rho_l}\right]_\beta + K\left[\frac{\partial (X_{i_0} X_{j_0})}{\partial \rho_l}\right]_\beta\right)$$

According to (40) and (41) we have

$$\beta\left[\frac{\partial \Delta E}{\partial \rho_l}\right]_\beta = -\frac{\Gamma}{\pi}(\Gamma + z)\left[\frac{\partial \Gamma}{\partial \rho_l}\right]_\beta - K\sum_{ij} X_{i_0} X_{j_0}\left[\frac{\partial \rho_i \alpha_i \rho_j \alpha_j t_{i_1 j_1}}{\partial \rho_l}\right]_\beta + \beta\left[\frac{\partial \Delta E}{\partial \rho_l}\right]_{\rho_p,\Gamma,\beta}.$$

The latter two expressions, when substituted into (57), yield the following simple expression for the chemical potential

$$\beta \Delta \mu_l = \beta\left[\frac{\partial \Delta E}{\partial \rho_l}\right]_{\rho_p,\Gamma,\beta} + \ln \alpha_l - \sum_{ij} \rho_i \alpha_i \rho_j \alpha_j t_{i_1 j_1}\left[\frac{\partial \ln g_{ij}^{HS}(\sigma_{ij})}{\partial \rho_l}\right]_\beta, \tag{58}$$

Expression for $\left[\frac{\partial\Delta E}{\partial\rho_l}\right]_{\rho_p,\Gamma,\beta}$ was obtained using (39) and (28), it reads

$$\beta\left[\frac{\partial\Delta E}{\partial\rho_l}\right]_{\rho_p,\Gamma,\beta} = -Kd_l\frac{e^{-z\sigma_l/2}}{\sigma_l\varphi_0\left(z\sigma_l\right)}X_{c0}$$

$$-K\sum_i\rho_i d_i\frac{e^{-z\sigma_i/2}}{\sigma_l\varphi_0\left(z\sigma_i\right)}\left(\left(\alpha_i T_i^\eta-\eta_i\right)\left[\frac{\partial\Delta_1}{\partial\rho_l}\right]_{\rho_p,\Gamma,\beta}+\frac{2\Delta}{\pi}\left(\alpha_i T_i^\xi-\xi_i\right)\left[\frac{\partial\eta^B}{\partial\rho_l}\right]_{\rho_p,\Gamma,\beta}\right)$$

$$+K\Delta_1 d_l\frac{e^{-z\sigma_l/2}}{\varphi_0\left(z\sigma_l\right)}+Kd_l^2\frac{e^{-z\sigma_l}}{\sigma_l\varphi_0\left(z\sigma_l\right)}+\left[\frac{\partial\Delta_1}{\partial\rho_l}\right]_{\rho_p,\Gamma,\beta}K\sum_i\rho_i d_i\frac{e^{-z\sigma_i/2}}{\sigma_i\varphi_0\left(z\sigma_i\right)}, \qquad (59)$$

where derivatives $\left[\frac{\partial\Delta_1}{\partial\rho_l}\right]_{\rho_p,\Gamma,\beta}$ and $\left[\frac{\partial\eta^B}{\partial\rho_l}\right]_{\rho_p,\Gamma,\beta}$ are given in the Appendix. Finally for the excess pressure ΔP one can use the following standard relation:

$$\beta\Delta P=\beta\sum_i\rho_i\Delta\mu_i-\beta\Delta A, \qquad (60)$$

Remarkable fact is that chemical potential and pressure are independent of $\left[\frac{\partial\Gamma}{\partial\rho_l}\right]_\beta$ and thus we don't need to solve any equations to obtain this derivative.

5 Summary and concluding remarks

In this paper we consider multi-component dimerizing Yukawa hard-sphere fluid. We present explicit analytical expressions for Helmholtz free energy, chemical potential, entropy and pressure of the system in terms of the Blum's scaling parameter Γ, which follows from the solution of the AMSA for the model with factorized Yukawa coefficients. In the latter case solution of the AMSA reduces to the solution of only one nonlinear algebraic equation for Γ. This feature enables the theory to be used in the description of the structure and thermodynamics of associating fluids with arbitrary number of components, including the limiting case of polydisperse fluids. We are currently studying the effects of polydispersity on the phase behavior of the polymer fluid combining the theory proposed here and dimer thermodynamic perturbation theory for polymers [34, 35].

6 Appendix

We present here expressions for the elements of the inverse matrix $\hat{\mathbf{M}}^{-1}$ and derivatives, which are needed to prove relation (41) and appear in the expression for the

chemical potential (58)

$$\left[\frac{\partial y_i}{\partial \Gamma}\right]_{\rho_p} = -\frac{2\Delta}{\pi\sigma_i}\xi_i y_i, \tag{61}$$

$$\left[\frac{\partial T_i^y}{\partial \Gamma}\right]_{\rho_p} = -\frac{2\Delta}{\pi\sigma_i}\xi_i T_i^y + \frac{2\Delta}{\pi\sigma_i}\xi_i \sum_k \rho_k \alpha_k t_{i_1 k_1} \frac{2\Delta}{\pi\sigma_k}\xi_k y_k \tag{62}$$

where y takes the values ξ,η or λ.

$$\left[\frac{\partial \chi_i}{\partial \Gamma}\right]_{\rho_p} = -\frac{2\Delta}{\pi\sigma_i}\xi_i \chi_i + \frac{2\Delta}{\pi}\xi_i. \tag{63}$$

$$\hat{\mathbf{M}}_{ki}^{-1} = \frac{e^{-\frac{z\sigma_i}{2}}}{1+\varphi_0\left(z\sigma_i\right)\sigma_i\Gamma}\left[\delta_{ik}\hat{\mathbf{I}} - \frac{\Delta z^2 + 2\pi\left(\Omega^\eta + \left(\frac{z}{2}+\Gamma+\frac{\pi\zeta_2}{2\Delta}\right)\Theta^\eta\right)}{\pi S}\tilde{\mathbf{c}}_k^T\tilde{\mathbf{d}}_i \right. \tag{64}$$

$$\left. + \frac{\Delta z^2\left(1-\Theta^\xi\right)}{\pi S}\tilde{\mathbf{e}}_k^T\tilde{\mathbf{f}}_i + \frac{2\Theta^\eta}{S}\tilde{\mathbf{c}}_k^T\tilde{\mathbf{f}}_i + \frac{\Delta z^2\left(\Omega^\xi + \left(\frac{z}{2}+\Gamma+\frac{\pi\zeta_2}{2\Delta}\right)\Theta^\xi\right)}{\pi S}\tilde{\mathbf{e}}_k^T\tilde{\mathbf{d}}_i\right],$$

where denominator

$$S = \Theta^\eta\left(2\Gamma + \frac{\pi}{\Delta}\zeta_2 + z + 2\Omega^\xi\right) + \frac{\Delta}{\pi}\left(z^2 + \frac{2\pi}{\Delta}\Omega^\eta\right)\left(1-\Theta^\xi\right). \tag{65}$$

$$\left[\frac{\partial \eta^B}{\partial \rho_l}\right]_{\rho_p,\Gamma,\beta} = \frac{\frac{\sigma_l}{2}\left(\frac{\sigma_l^2}{3}\eta^B + X_{c0}\right)\left(z^2+\frac{2\pi}{\Delta}\Omega^\eta\right) - \frac{\pi}{2\Delta}\Theta^\eta L_l}{S}, \tag{66}$$

$$\left[\frac{\partial \Delta_1}{\partial \rho_l}\right]_{\rho_p,\Gamma,\beta} = \frac{-\left(2\Omega^\xi + 2\Gamma + z + \frac{\pi\zeta_2}{\Delta}\right)\sigma_l\left(\frac{\sigma_l^3}{3}\eta^B + X_{c0}\right) - \left(1-\Theta^\xi\right)L_l}{S}, \tag{67}$$

where

$$L_l = 2\eta^B\sigma_l^2\left(1+\frac{\pi\zeta_2\sigma_l}{6\Delta}\right) + \frac{\pi\sigma_l^3}{3\Delta}\left(\Omega^\lambda + \Delta_1\Omega^\eta + \frac{2\Delta}{\pi}\eta^B\Omega^\xi\right) + 2X_{c0}. \tag{68}$$

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